

# Zirconia Based / Nafion Nanocomposite Membranes for Fuel Cell Applications

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**Abstract** -The nanoparticles of zirconium oxide, sulfated zirconia and phosphated zirconia were used to modify Nafion membrane in order to improve the water retention, thermal stability, proton conductivity and methanol permeability. The modified Nafion nanocomposite membranes were used for high temperature fuel cell between 120-140°C. The inorganic nanoparticles were incorporated within Nafion by recast, swelling-impregnation and ion exchange methods. The inorganic nanoparticles were characterized by XRD, BET, FTIR, TGA, DSC, SEM and TEM, while nanocomposite membranes were characterized for water uptake, ion exchange capacity, methanol permeability, and proton conductivity. Pristine ZrO<sub>2</sub>, sulfated and phosphated ZrO<sub>2</sub> were successfully synthesized. The particle sizes ranged from 10 nm to 30 nm, with good dispersity in the membrane. The conductivity of the Nafion / 5% sulfated zirconia membrane exceeded 0.103 S/cm at room temperature and has the highest water uptake of 35%. On the other hand, Nafion / 15% sulfated zirconia was found to have the highest ion exchange capacity of 1.42 meq.g<sup>-1</sup>.

**Keywords:** Zirconium oxide, Sulfated zirconia, Phosphated zirconia, Proton conductivity, Nafion, Fuel cell.

## 1. Introduction

Fuel cell technology is expected to become one of the key technologies of the 21<sup>st</sup> century both for stationary and vehicular applications (Savadogo, 2004; Neburchilov et al., 2007).

Proton exchange membrane fuel cells (PEMFC) with hydrogen as a fuel attracted the most attention due to the high electrochemical reactivity, the efficiency achievable is higher than in power plants or internal combustion engines and practically zero pollution level. However, issues regarding the appropriate and safe transportation and storage of hydrogen were a strong impediment for the hydrogen fuel cells commercialization (Scott et al., 1999; Nunes et al., 2002).

Direct methanol fuel cell (DMFC) uses liquid methanol has several advantages including high efficiency, very low emissions, lower weight and volume compared with indirect fuel cells, a potentially renewable fuel source (Scott et al., 1998; Choi et al., 2002). Methanol is a liquid at room temperature; as a consequence, the existing gasoline distribution infrastructure can be used.

Proton conducting membrane is the key component of a fuel cell system. A membrane with high proton conductivity (typically  $\geq 10^{-2}$  S/cm), chemical and thermal stability, and mechanical strength are required. Perfluorosulfonated membranes are widely used as proton conductor including Nafion series (DuPont), with Nafion 117 is the preferred membrane for DMFC, Dow XUS (Dow Chemical Co.) and Flemion (Asahi Glass Co.). Perfluorinated membranes are expensive, because of the complication and the longevity of the manufacture process (Savadogo, 1998), which includes strongly toxic and environment-unfriendly intermediate (Kerres, 2001). The high methanol permeability in

these membranes from anode to cathode, known as methanol crossover, affects severely the DMFC performance.

The operation of PEMFC at temperature above 140°C is receiving world-wide attention because fuel selection remains straightforward, where a number of fuels, including reformed hydrogen with high CO content and light hydrocarbons (alcohol, natural gas, propane, etc.) can be used. Accordingly, the anode catalyst poisoning by CO is less important and the kinetics of fuel oxidation will be improved and the efficiency of the cell significantly enhanced. High temperature cell operation will contribute in reducing the complexity of the hydrocarbon fuel cell system. Some other advantages of operating PEMFC at high temperature are: a reduction in the use of expensive catalysts; and minimization of the problems related to electrode flooding.

The organic / inorganic nanocomposite proton conductors are developed to overcome the breakdown of the actual state-of-the-art membranes (i.e. PFSA membranes). Thus, increasing the operating temperature above 100°C, reduced methanol permeability (methanol crossover), increasing the water retention and also increasing the mechanical and thermal stability of the composite membranes (Mokrani, 2012).

## **2. Experimental**

Zirconium oxide was prepared and modified by sulfonation or phosphonation. The prepared zirconia was incorporated in Nafion by recast, swelling and ion exchange methods. Zirconia oxide, sulphated zirconia and phosphate zirconia were characterized, then the nanocomposite membrane was characterized for fuel cell applications.

### **2. 1. Preparation of Zirconium Oxide (ZrO<sub>2</sub>)**

The ZrO<sub>2</sub> nanoparticles was prepared by precipitation method, zirconium oxychloride hydrate (ZrOCl<sub>2</sub>. 8H<sub>2</sub>O) and ammonia (NH<sub>3</sub>) were used as starting materials. All the chemicals were used as received without any further purification. Zirconium hydroxide's precipitation (Zr(OH)<sub>4</sub>) was obtained by adding an NH<sub>4</sub>OH aqueous solution drop wise to the aqueous solution of 0.2M ZrOCl<sub>2</sub>.8H<sub>2</sub>O at room temperature while vigorously stirring until the desired pH of 10 was reached (Hara and Miyayama, 2004). The precipitate was divided into two parts. The one part of the precipitate was washed with deionized water until the chlorine ions (Cl<sup>-</sup>) were not detected by the silver nitrate (AgNO<sub>3</sub>) test and filtered by filter paper to obtained wet powders Zr(OH)<sub>4</sub>. The wet powder was dried in an oven at 100°C overnight. Zirconia nanopowder (ZrO<sub>2</sub>) was obtained through calcinations of the dried zirconium hydroxide at 600°C for 6 hours. The remaining part of the precipitate formed as described above was aged in the mother liquor (Adamski et al., 2006) for 48 hours at room temperature, after which it was filtered, then washed and calcinated according to the first one's procedure.

### **2. 2. Preparation of Sulfated Zirconia (S-ZrO<sub>2</sub>)**

Sulfated zirconia nanopowder was prepared by vigorously stirring the dried ZrO<sub>2</sub> nanopowder obtained in 0.5M H<sub>2</sub>SO<sub>4</sub> for 30 minutes at room temperature. The resulting solid was filtered and dried at 100°C for 48 hours. The dried S-ZrO<sub>2</sub> nanopowder was then calcined at 600°C for 2 hours and the resulting particles were crushed with a mortar and pestle (Hara and Miyayama, 2004).

### **2. 3. Preparation of Phosphated Zirconia (P-ZrO<sub>2</sub>)**

The phosphated zirconia (P-ZrO<sub>2</sub>) nanoparticle was obtained by impregnation of an aqueous solution of diammonium hydrogen phosphate onto pure ZrO<sub>2</sub> nanoparticle, using minimal amount of the impregnating solution (25 ml/g) to give 6 wt.% PO<sub>4</sub><sup>-3</sup> (Mekhemer and Ismail, 2000). A portion of the ZrO<sub>2</sub> nanopowder was dissolved in aqueous solution of diammonium hydrogen phosphate solution with a magnetic stirrer at room temperature for 30 minutes. The P-ZrO<sub>2</sub> nanoparticle suspension obtained was filtered and dried at 100°C for 48 hours, the dried P-ZrO<sub>2</sub> was then calcined at 600°C for 2 hours. The resulting particles were crushed with mortar and pestle.

## **2. 4. Preparation of Nanocomposite Membranes**

The zirconia based / Nafion nanocomposite membranes were prepared using three different methods, namely, recast, swelling-impregnation and ion exchange techniques.

### **2. 4. 1. Recast Method Using Isopropyl Alcohol (IPA)**

Nafion solution (5 wt.%, 1100 EW) and IPA were mixed in an ultrasonic bath for 5 minutes, with a volume ratios of 1:2 (Nafion solution to IPA). 5% to 15% of  $ZrO_2$ , S- $ZrO_2$  and P- $ZrO_2$  nanopowders were added to the mixture. The mixture was then mixed ultrasonically for 20 minutes. The mixture was recast in glass petri dish, dried at 80°C for 24 hours in an air oven, followed by 160°C for 30 minutes. The recast Nafion film was pulled off from petri dish by adding a small amount of deionised water. The recast Nafion / zirconium based nanocomposite membrane was treated according to the standard procedure by boiling in 3 vol.% hydrogen peroxide ( $H_2O_2$ ) for 1 hour to remove the organic impurities, followed by washing with boiling deionised water for 30 minutes. The membrane was then boiled in 1M  $H_2SO_4$  for 1 hour to remove the inorganic impurities and also to complete the protonation and then washed with water for 30 minutes. Washing with water was repeated several times to remove any traces of acidity. Finally the membrane was kept in water prior to measurements.

### **2. 4. 2. Recast Method Using N, N-dimethylformamide (DMF)**

Nafion solution (5 wt.%, 1100 EW) and DMF were mixed and stirred at room temperature for 2 hours, then in an ultrasonic bath for 30 minutes, with a volume ratios of 1:5 (Nafion solution to DMF). Appropriate amount of additive i.e.  $ZrO_2$ , S- $ZrO_2$  and P- $ZrO_2$  nanopowders were added to the mixture. The resulting solution was poured onto a piece of flat glass, and placed into an oven at 80°C for 12 hours to remove solvent, followed by 160°C for 30 minutes. The membranes were then removed by peeling off from the glass plate and treated according to standard method above.

### **2. 4. 3. Ion Exchange Method**

The composite membranes were prepared using Nafion 117 film. Nafion films were purified by boiling in 3% hydrogen peroxide for 1 hour, then rinsed with boiling water, and treated in boiling 1M sulphuric acid for 1 hour and finally rinsed again with boiling water several times. Zirconia / Nafion 117 nanocomposite membrane was prepared by means of ion exchange of zirconium ions into the Nafion 117. The Nafion 117 membrane was soaked in  $ZrOCl_2/2$ -propanol solution at 80°C for 24 hours. The membrane was removed, blotted, and placed in 2-propanol/ $H_2O$  solution for 2 hours at 80°C. After the acid hydrolysis and condensation reactions, the membrane was removed and dried at 80°C for 24 hours and then at 110°C for 2 hours. For sulfated zirconia / Nafion 117, the prepared membrane with ion exchange method was boiled in 5M  $H_2SO_4$  solution at 60°C for 1 hour to sulfate the formed  $ZrO_2$  nanoparticles, and finally rinsed in water. The phosphated zirconia / Nafion 117 was prepared via an ion exchange reaction involving  $ZrO^{2+}$  ions followed by precipitation of phosphated zirconia nanoparticles by immersion of the membrane in diammonium hydrogen phosphate acid.

### **2. 4. 4. Swelling-impregnation Method**

Nafion-impregnated nanocomposite membranes were prepared by maximum swelling of Nafion 117 film in methanol solution to open the pores of Nafion. The required amount (5 to 15 wt.%) of  $ZrO_2$ , S- $ZrO_2$  and P- $ZrO_2$  nanoparticles suspension in methanol were added to the petri dish. The composite membranes were repeatedly impregnated up to 5 times at room temperature. In order to remove any air from the membrane pores, the suspension and the membranes were heated up to 100°C, then slowly cooled down to room temperature and kept in the solution 24 hours. After drying the membranes were stored in deionized water.

## 2. 5. Characterization of Nanocomposite Membranes

The zirconia based / Nafion nanocomposite membranes were characterized for structural, thermal and surface analysis. Also the membranes were characterized for their conductivity, water uptake, and ion exchange capacity.

### 2. 5. 1. Conductivity Measurement

The ionic conductivities of nanocomposite membranes were measured in a two electrodes cell using ac impedance spectroscopy at different temperatures and relative humidity (RH). An Autolab PGSTAT302 was used at galvanostatic mode with ac current amplitude of 0.1 mA over frequencies ranging from 1 MHz to 10 Hz, under the 100% RH for 25-80°C and 50% RH for 85-90°C. Using a Bode plot, the frequency region over which the impedance had a constant value was checked, and the resistance was then obtained from Nyquist plot. The ionic conductivity ( $k$ ) was calculated according to Equation (1):

$$k = \frac{L}{RWd} \quad (1)$$

where  $R$  is the obtained membrane resistance,  $L$  is the distance between the two electrodes (1cm) and  $W$  and  $d$  are the width (2 cm) and thickness of the membrane.

### 2. 5. 2. Water Uptake (Wup %)

The water uptake of the membrane was determined by immersing the membrane into water at room temperature for 24 hours. The membrane taken out, wiped with tissue paper and weighed immediately. Water uptake will be calculated according to Equation (2):

$$\text{Wup}(\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad (2)$$

where  $\text{Wup}$  is the percentage of water uptake,  $m_{\text{wet}}$  is the weight of a swollen membrane immersed into water at room temperature for 24 hours and  $m_{\text{dry}}$  is the weight of the same membrane after being dried.

### 2. 5. 3. Ion Exchange Capacity (IEC)

The ion exchange capacity (IEC) was defined as the ratio between the numbers of the surface ionogenic groups (mmol) and the weight of the dry materials (Dimitrova et al., 2002). A titration technique was used to determine the IEC of the membranes. Firstly, the membrane was dried at 60°C for 24 hours and measured the weight. The dried membranes in the proton form ( $\text{H}^+$ ) were immersed in 60 ml of 1M NaCl at 50-60°C for 24 hours to exchange the  $\text{H}^+$  ions with  $\text{Na}^+$  ions. The 60 ml of  $\text{H}^+$  ions solution were titrated with a 0.01M NaOH solution using phenolphthalein as the endpoint indicator (Yoon et al., 2002).

## 3. Results

### 3. 1. XRD Analysis

Figure 1 show the diffraction pattern of the as-prepared  $\text{ZrO}_2$ , S- $\text{ZrO}_2$  and P- $\text{ZrO}_2$  powder. The crystallinity of the samples is evidenced by sharper diffraction peaks at respective diffraction angles. All the samples exhibit the monoclinic phase and the major peaks appeared at 24.4°, 28.2°, 31.5°, 34.5° and 62.3° (Jiao et al., 2003 and Ray et al., 2000), while the tetragonal phase peaks appeared at 30.2°, 50.2°, 59.3° and 60.2° (Bondars et al., 1995 and Zhou et al., 2006). The strongest diffraction peak of monoclinic structure which appeared at  $2\theta = 28.2^\circ$  is due to the (111) plane and the major peak for the tetragonal structure is seen at  $2\theta = 30.5^\circ$  corresponds to the (101) plane. The XRD patterns of the samples synthesised by aging method are shown in Figure 2. All the samples showed

similar patterns at  $30.2^\circ$ ,  $50.2^\circ$  and  $60.2^\circ$   $2\theta$  which are characteristics of zirconium in a tetragonal phase. The peaks at  $30.2^\circ$ ,  $50.2^\circ$  and  $60.2^\circ$  correspond to the planes (h k l) at 101, 112 and 211 respectively. These XRD patterns show that these materials are amorphous as evident by peaks and humps. From these results it can be deduced that the slow aging of samples favoured the tetragonal structure growth.

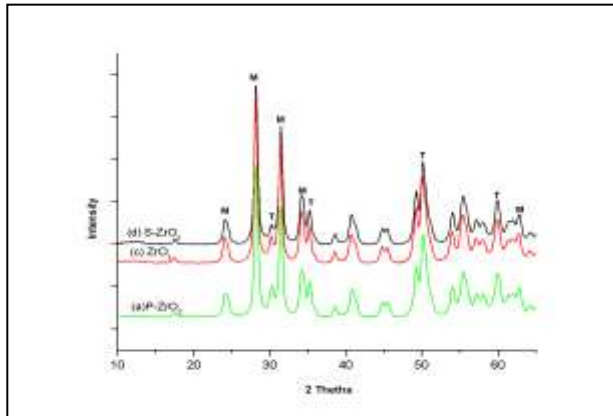


Fig. 1. XRD patterns of  $ZrO_2$ ,  $S-ZrO_2$  and  $P-ZrO_2$  powder.

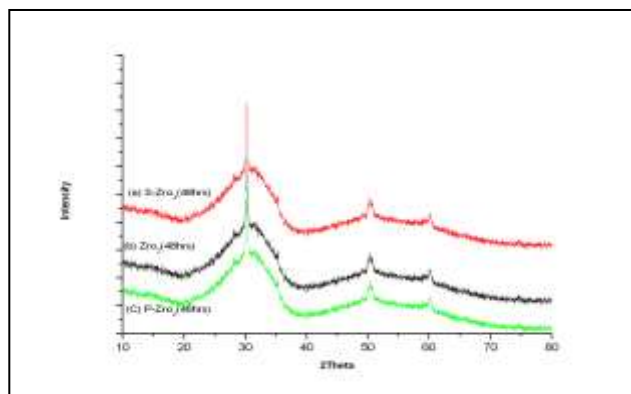


Fig. 2. XRD patterns of  $ZrO_2$ ,  $S-ZrO_2$  and  $P-ZrO_2$  powder at 48 hours aging.

The X-ray diffraction analysis for the nanocomposite membranes developed by recasting, ion exchange and impregnation method compared to plain recast Nafion membranes are shown in Figure 3. The XRD results of nanocomposite membrane with that of plain recast Nafion membrane shows a very similar broad diffraction features at Bragg angles ( $2\theta$ ) of the  $12-22^\circ$  (Moore and Martin, 1988). Also, Figure 3 shows the broad peak around  $2\theta = 40^\circ$  which is associated with the fluorocarbon chains of Nafion film indicating the poor crystallinity of Nafion matrix (Mauritz and Payne, 2000). The Nafion / 10%  $S-ZrO_2$  (recast) nanocomposite membranes showed some extra peaks as compared to Nafion membrane corresponding to  $S-ZrO_2$  nanoparticles. However, the Nafion / 10%  $S-ZrO_2$  (ion exchange) nanocomposite membranes showed a pattern essentially identical to Nafion membrane due to the low loading of  $S-ZrO_2$  nanoparticles. The Nafion / 10%  $S-ZrO_2$  (impregnation) nanocomposite membranes show the peaks of the considered  $S-ZrO_2$  powder confirming the presence of inorganic compound within the Nafion membrane.

Figure 4 present the XRD results of Nafion / 10%  $ZrO_2$ , Nafion / 10%  $P-ZrO_2$  and Nafion / 10%  $S-ZrO_2$  nanocomposite membranes for un-aged samples, which have very similar reflections, showing there is no crystalline change of mixing these nanoparticles within the membranes. However, all the samples presents a sharper peak at  $2\theta = 15^\circ$  due to the presence of bigger clusters with respect to the Nafion membrane (Sacc`a et al., 2006).

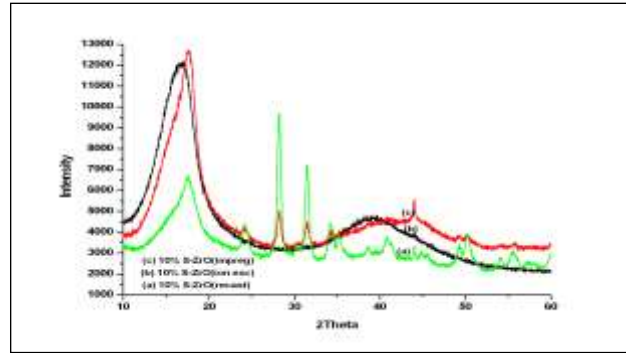


Fig. 3. XRD patterns of (a) Nafion/10% S-ZrO<sub>2</sub> (recast), (b) Nafion/10% S-ZrO<sub>2</sub> (ion exc) and (c) Nafion/10% S-ZrO<sub>2</sub> (impregnation) nanocomposite membranes

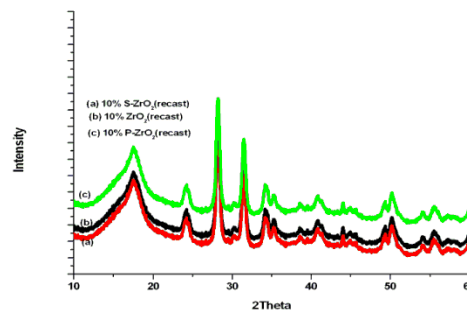


Fig. 4. XRD patterns of (a) Nafion/10% S-ZrO<sub>2</sub>, (b) Nafion/10% ZrO<sub>2</sub> and (c) Nafion/10% P-ZrO<sub>2</sub> recast nanocomposite membranes (un-aged)

### 3. 2. SEM Analysis

Figure 5 shows the SEM images of un-aged and aged ZrO<sub>2</sub>. The aged nanoparticles consist of primary units of very small dimensions, around 200 nm with the reduced agglomeration when compared to un-aged nanoparticles (Fig. 5(a)), while the un-aged nanoparticles (Fig. 5(b)) is in the form of agglomerates which exhibit a wide size distribution with dimensions varying to around 1 microns. From Figure 5 it can be concluded that by aging the nanoparticles can reduce the agglomeration as well as reducing the particles size.

Figure 6 shows SEM micrographs of S-ZrO<sub>2</sub> nanoparticles un-aged and aged at 48 hours, as well as P-ZrO<sub>2</sub> aged at 48 hours. From the SEM images of S-ZrO<sub>2</sub> (Fig. 6 (a) and (b)) the particles were less agglomerated, which means that the S-ZrO<sub>2</sub> suspension was well dispersed. It can be concluded that the modification of ZrO<sub>2</sub> nanoparticles with sulphuric acid leads to the smaller particles. The aged S-ZrO<sub>2</sub> nanoparticles present a quite different surface morphology with a slight aggregation. Figure 6 (c) shows SEM micrograph of P-ZrO<sub>2</sub> nanoparticles aged at 48 hours, which consists of spherical nanostructures. It can be seen that the addition of diammonium hydrogen phosphate acid increases the particle size when compared with ZrO<sub>2</sub> nanoparticles.

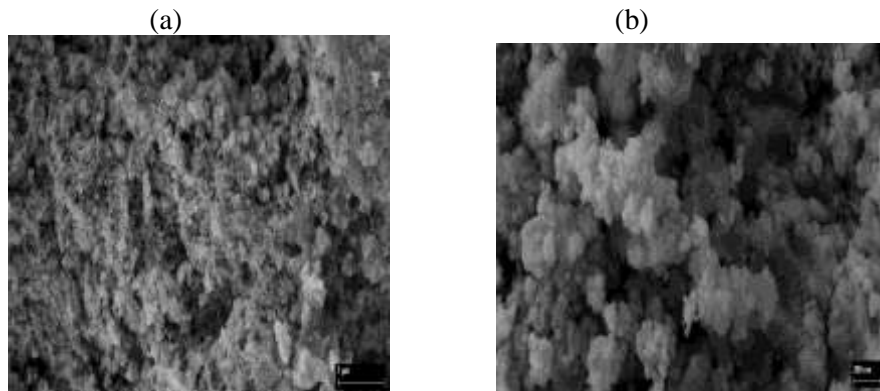


Fig. 5. SEM image of the  $ZrO_2$  nanoparticles: (a) aged at 48 hours and (b) un-aged.

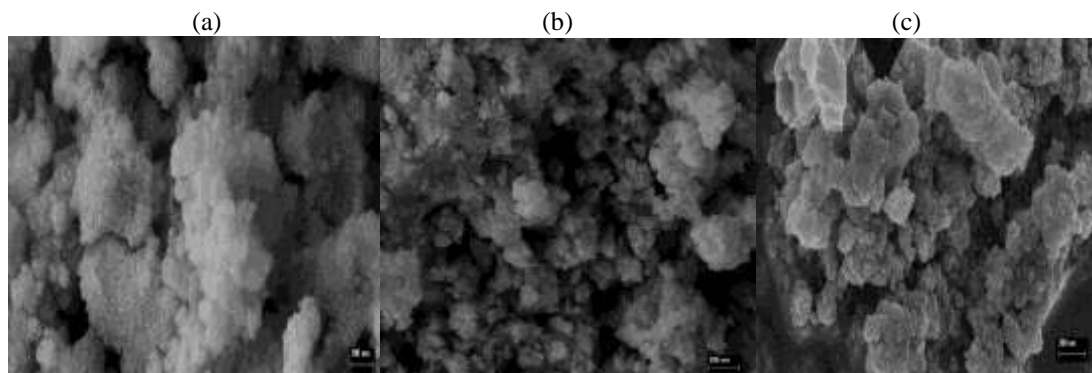


Fig. 6. SEM image; (a) S- $ZrO_2$  aged at 48 hours, (b) S- $ZrO_2$  un-aged, and (c) P- $ZrO_2$  aged at 48 hours.

### 3. 3. TEM analysis

Figure 7 presents the TEM image of  $ZrO_2$  nanoparticles of aged and un-aged nanoparticles. It can be seen that size distribution of un-aged  $ZrO_2$  particles are narrowly dispersed with particle size range from 20-30 nm, having a lesser agglomeration, and this can be attributed to the calcination temperature. Also the un-aged  $ZrO_2$  image indicates that the particles presented a uniform spherical shape. TEM images for the aged  $ZrO_2$  shows fine-particle morphologies with the particle size range from 11-25 nm with lesser particle agglomeration.

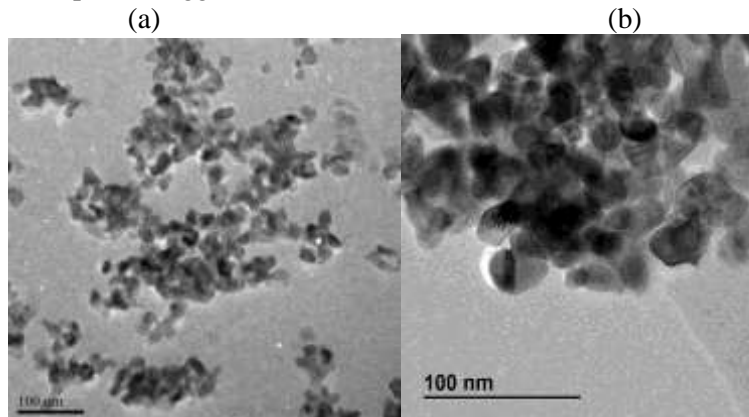


Fig. 7. TEM image of  $ZrO_2$ ; (a) un-aged and (b) aged at 48 hours.

### 3. 4. Ion Exchange Capacity (IEC) and Water Uptake

Figure 8 shows the results of ion exchange capacity and water uptake for nanocomposite membranes made by recast method. The results shows that the Nafion / 15% S- $ZrO_2$  nanocomposite

membrane was the most acidic membrane when compared with the other nanocomposite membranes, having the highest IEC value of  $1.42 \text{ meq.g}^{-1}$ . The results also show that increasing the amount of inorganic can enhance the water uptake, which may be caused by water being captured inside zirconia nanoparticles or in gaps between zirconia and Nafion membrane.

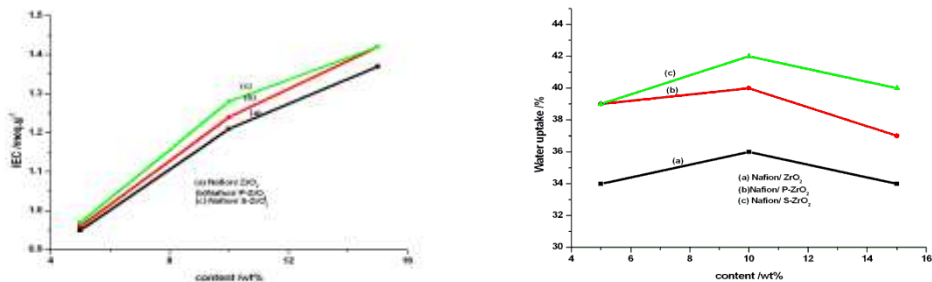


Fig. 8. Ion exchange capacity (IEC) and water uptake of nanocomposite membranes by recast method.

### 3. 5. Proton Conductivity

The results in Table 1 shows the proton conductivity of Nafion 117 membrane is  $1.4 \times 10^{-2} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$  whereas that of the Nafion/ 5% P-ZrO<sub>2</sub> nanocomposite membranes is  $4.3 \times 10^{-3} \text{ S cm}^{-1}$  which is the lowest conductivity. It can be seen in Table 1 that the highest conductivity at room temperature is for Nafion/ 5% S-ZrO<sub>2</sub> nanocomposite membrane with a value of  $0.1037 \text{ S cm}^{-1}$ , which make it the best candidate to be added to Nafion polymer.

Table. 1. Proton conductivity of different membranes at  $25^\circ\text{C}$ .

Samples	Proton conductivity ( $\text{S/cm}^{-1}$ ) at $25^\circ\text{C}$
Nafion/ 5% ZrO <sub>2</sub>	0.0413
Nafion/ 5% P-ZrO <sub>2</sub>	0.0043
Nafion/ 5% S-ZrO <sub>2</sub>	0.1037
Nafion 117	0.015
Plain recast Nafion	0.014

### 4. Conclusion

The nanocomposite membranes were found to have higher water uptake and higher acidic which makes them suitable candidates for fuel cell applications. The proton conductivity was obtained to be higher with less resistance, with a value of  $0.1037 \text{ S/cm}$  at room temperature for Nafion/5% S-ZrO<sub>2</sub> nanocomposite membranes and  $0.0413 \text{ S/cm}$  for Nafion/5% ZrO<sub>2</sub> nanocomposite membranes which agreed with properties for fuel cell application. It was shown from the results above that the IEC of modified membrane increased with increasing additive content. Zirconium oxide modified by diammonium hydrogen phosphate solution resulted in poor proton conductivity at lower temperature.

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